

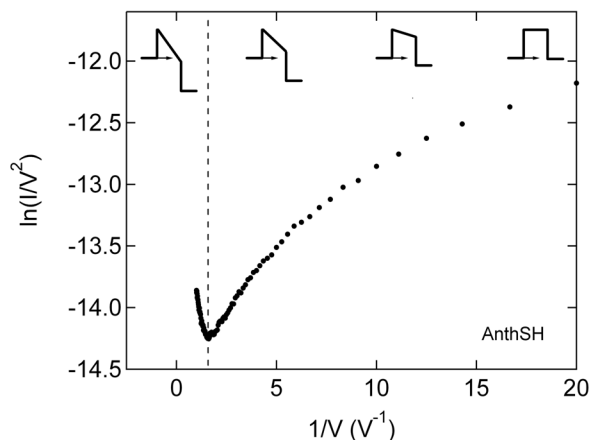
## Charge Transport in Molecular Electronic Systems

*Molecular Electronics envisions that the nonlinear characteristics of individual or small ensembles of molecules will provide the active element in future electronic devices enabling some of the high-cost semiconductor fabrication processes to be replaced by low-cost chemical synthetic methods. A detailed understanding of charge transport across metal-molecule-metal junctions, the fundamental building block of a molecular electronic device, is paramount for molecular electronics to transition from a research endeavor into a viable technology. Our efforts have focused on the fundamental physical measurements that will provide the needed insight to enable the rational design of molecular electronic devices.*

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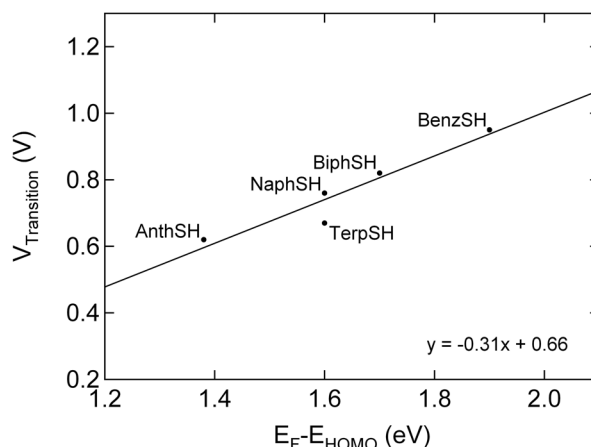
By combining direct charge transport measurements with photoelectron spectroscopy NIST researchers are able to correlate the charge transport properties of  $\pi$ -conjugated molecules with their effective band lineup. Conducting probe atomic force microscope and crossed-wire tunnel junction measurements on metal-molecule-metal junctions reveal a transition from tunneling through a trapezoidal barrier to tunneling through a triangular barrier for a series of  $\pi$ -conjugated molecules as shown in the Figure 1.

**Figure 1. Charge transport characteristics of an anthracenethiol junction.** The barrier diagrams schematically represent the tunneling event as the bias is increased. The dotted line corresponds to the transition from a trapezoidal to a triangular barrier.



Additionally the position of this tunneling barrier transition correlates strongly with the energy offset between the metal electrode's Fermi level ( $E_F$ ) and the energy of the molecule's highest occupied molecular orbital ( $E_{HOMO}$ ) as measured by ultraviolet photoemission spectroscopy (Figure 1, bottom). We refer to the energy offset ( $E_F - E_{HOMO}$ ) as the band lineup in analogy to conventional metal-semiconductor contacts. This study provides one of the first demonstrations linking the charge transport properties of a metal-molecule-metal junction with the measured band lineup of the system.

**Figure 2. Transition voltage as a function of the  $E_F - E_{HOMO}$  energy difference for each of the molecules studied. Also shown is a linear fit to the data.**



**Future Plans:** We have focused these initial studies on systems incorporating Au-thiolate linkages since they are the most common metal-molecule contact employed in molecular electronics research. Future studies will examine other metal electrodes and linker chemistries to elucidate their role in controlling band lineup.

As academic, government, and industrial laboratories pursue the development of molecular electronic devices, the approach described herein provides important insights which can be applied to optimize the charge transport properties of such devices.